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Title: Low grade propylene polymerization method

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Brief Description of the Drawing

The drawing is a graph which shows the relation between the conversion ratio and the time varying depending on whether or not solvent is present.

Detailed Explanation of the Invention

The present invention relates to an improved process for producing dimer ~ tetramer olefin consisting mainly of nonene by low grade propylene polymerization by use of a boric fluoride complex as a catalyst, and it is characterized in that this reaction is conducted by using, as solvent, paraffin ✓ or part of the low grade propylene polymerization products.

The inventors of the present invention have succeeded in obtaining hexene, nonene and dodecene in high yield by using, as a catalyst, in low grade propylene polymerization, a boric trifluoride complex where an aliphatic alcohol, ether or acid is independently a ligand or the former two are ligands at the same time.

The object of the present invention lies in increasing the rate of reaction and simultaneously improving yield of dimer ~ tetramer and,

further, changing the distribution thereof, thus to improve the proportion of trimer being the main product, by using, as solvent, at the time of this low grade polymerization, 3 ~ 15C paraffin or polymer of more than tetramer, of the low grade propylene polymerization products.

In the reaction in the absence of solvent using, as a catalyst, the aforesaid boric trifluoride complex, the yield of dimer ~ tetramer and the distribution thereof are almost defined by the conversion ratio of the reaction and no substantial difference is brought about by changing the reaction temperature, reaction pressure, reaction time and catalyst amount.

Thus, the use of 3 ~ 15C paraffin or polymer of tetramer or more of the low grade propylene polymerization products, as solvent, according to the process of the present invention, makes the yield of dimer ~ tetramer higher, in any conversion ratio, than the case where solvent is not used, and product distribution more advantageous to trimer being the main product can be obtained. Also, with the other conditions being the same, the time required for achieving the same conversion ratio is shorter than the reaction in the absence of solvent.

The aforesaid effect is attributable to the solvent enhancing solubility of the catalyst in the propylene phase. Namely, in the above-mentioned low grade propylene polymerization using, as a catalyst, a boric trifluoride complex, the propylene present in the gas-phase can be ignored when using, in the absence of solvent, a reaction vessel having an appropriate volume for raw material propylene. Thus, the reaction system can be regarded as a heterogeneous system which consists of a liquid-phase A mainly composed of propylene and a polymer thereof and a liquid-phase B mainly composed of the catalyst, and the catalyst exhibits a considerable solubility with respect to the A-phase. Hence, there are reactions which occur, respectively, in the A-phase by the action of the catalyst dissolved in the A-phase and in the B-phase by the propylene dissolved in the B-phase.

The reaction in the B-phase is more advantageous to the production of a high polymer than the reaction in the A-phase.

Whereas in the case of adding the previously mentioned solvent, the solvent forms a homogeneous phase A' along with propylene and a polymer thereof. The solubility of the catalyst in the A'-phase is greater than in the A-phase and this results in increasing the catalyst participating effectively in the reaction intended by the present invention and, also, remarkably decreasing the B-phase or causing it to cease to exist depending on the reaction conditions, thus to control the production of a high polymer.

The process of the present invention is explained below in detail.
3 ~ 15C paraffin and any one of the polymers of tetramer or more of the lower polymers of propylene or a mixture of two or more of such polymers is used as solvent. It does not matter whether this paraffin is branched. The solvent amount in the reaction system is usually set so as to be the same as or less than the amount of raw material propylene.

The effect of the above solvent can be recognized when using, as a catalyst, any of the boric trifluoride complexes as shown below. Namely, the catalyst is a boric trifluoride complex where the aliphatic alcohol, ether and acid represented respectively by ROH, ROR' and RCOOH (R and R' denote a 1-3C alkyl group which may be the same or different from each other) are independently a ligand or two of them are ligands at the same time.

The sufficient amount of this catalyst used is usually 15 weight per cent or less, as boron trifluoride, based on the raw material propylene. The increase in the catalyst amount brings about the enhancement of the rate of reaction, but it exerts almost no influence on the distribution of products. The reaction temperature can be selected from the temperatures in the range of room temperature to 200°C, and a desirable result can be obtained, in particular, in the range of 70 ~ 100°C. The reaction pressure may be a

vapor pressure determined by the reaction system composition. The reaction can be conducted either by a batch process, using a stirring tank type reactor, or by a continuous process with a stirring tank type or pipe type reactor.

The following examples are presented to illustrate the present invention.

Example 1

Into an 200 ml rotary stirring type autoclave made of stainless steel, 50g of propylene and 7.3g of $\text{BF}_3 \cdot 2 \text{CH}_3 \text{OH}$ (7.5% calculated as BF_3 based on the propylene) were charged and a batch type reaction was conducted at 90°C . Further, a reaction was carried out by adding 30g of propane or n-dodecane to the same reaction system as the above thus to obtain the relation between the reaction time and the conversion ratio as shown by the drawing. Namely, the time required for attaining a 60% conversion ratio was 90 minutes in the absence of solvent, 54 minutes in the presence of propane and 60 minutes in the presence of n-dodecane. The distribution of products at a 60% conversion ratio was as shown below:

Solvent	Distribution of Products (weight %)			
	dimmer	trimer	tetramer	others
not present	5.2	56.2	29.5	9.1
propane	7.1	62.7	25.2	5.0
n-dodecane	6.4	61.0	27.2	5.4

Example 2

With the same autoclave as used in Example 1, 50g of propylene was polymerized in a similar manner in the presence of 8.6g of $\text{BF}_3 \cdot \frac{1}{2} \text{CH}_3 \text{OH}$ ($\text{C}_2\text{H}_5)_2\text{O}$ [7.5% calculated as BF_3 based on the propylene] and 30g of n-hexane at 80°C for 100 minutes. As a result, the conversion ratio was

55.1%, and the selectivity of each of the dimer, trimer, tetramer and the others was 7.2, 63.5, 24.5 and 4.8 weight per cent. Similar reaction was conducted in the absence of solvent and consequently the time required for attaining the same conversion ratio was 170 minutes, and the selectivity at that time of each of the dimer, trimer, tetramer and the others was 6.5, 54.6, 32.8 and 6.1 weight per cent.

Example 3

With the same autoclave as used in Example 1, 50g of propylene was polymerized in a similar manner in the presence of 7.8g of $\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$ [7.5% calculated as BF_3 based on the propylene] and 30g of propylene pentamer hydrogenated product at 80°C for 100 minutes. As a result, the conversion ratio was 43.4%, and the selectivity of each of the dimer, trimer, tetramer and the others was 6.8, 65.0, 25.1 and 3.1 weight per cent. Similar reaction was conducted in the absence of solvent and consequently the time required for attaining the same conversion ratio was 140 minutes, and the selectivity at that time of each of the dimer, trimer, tetramer and the others was 3.0, 60.8, 28.5 and 7.7 weight per cent.

Example 4

With the same autoclave as used in Example 1, 50g of propylene was polymerized in a similar manner in the presence of 7.3g of $\text{BF}_3 \cdot 2\text{CH}_3\text{OH}$ [7.5% calculated as BF_3 based on the propylene] and 30g of a mixture of polymers of tetramer or more of propylene (including tetramer ~ octamer, and the proportion of tetramer, pentamer, hexamer, heptamer and octamer was 39.5, 39.4, 13.2, 5.5 and 2.3 weight per cent) at 80°C for 240 minutes. As a result, the conversion ratio was 63.0%, and the selectivity of each of the dimer, trimer, tetramer and the others was 9.9, 60.8, 25.3 and 4.0 weight per cent. Similar reaction was conducted in the absence of solvent and

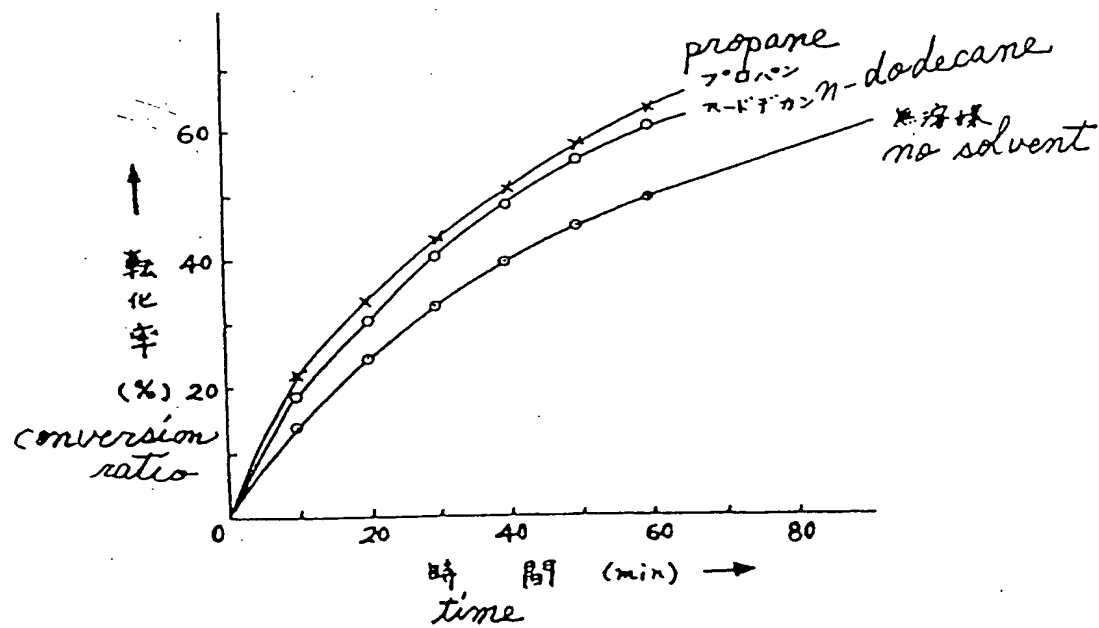
consequently the time required for attaining the same conversion ratio was 290 minutes, and the selectivity at that time of each of the dimer, trimer, tetramer and the others was 4.1, 56.8, 30.1 and 9.1 weight per cent.

Example 5

Using a 1ℓ rotary stirring autoclave made of stainless steel, a reaction was conducted by continuous system. As a catalyst, a composition which is composed of 44 weight per cent of boron trifluoride and the rest being methylisopropyl ether and methanol in the ratio of 2:1 was used in the amount of 4 weight per cent calculated as boron trifluoride based on the propylene. A propylene pentamer was used as solvent in the amount of 60 weight per cent based on the propylene and a reaction was conducted under the conditions of 80°C temperature, 30kg/cm² pressure and average residence time of 10 minutes. As a result, the conversion ratio was 65.4% and the selectivity of each of the dimer, trimer, tetramer and the others was 9.5, 60.6, 25.1 and 4.8 weight per cent. Similar reaction was conducted in the absence of solvent and consequently the average residence time required for attaining the same conversion ratio was 13 minutes, and the selectivity at that time of each of the dimer, trimer, tetramer and the others was 2.6, 48.6, 36.1 and 12.7 weight per cent.

What is claimed:

1. Low grade propylene polymerization process characterized by using, as solvent, 3 ~ 15C paraffin or polymer of tetramer or more of the propylene low grade polymerization products in obtaining dimer ~ tetramer by polymerizing propylene using, as a catalyst, a boric trifluoride complex where the aliphatic alcohol, ether, acid and ester represented by the general formulae ROH, ROR', RCOOH and RCOOR respectively (R and R' denote the an 1-3C alkyl which may be the same or different from each other) are independently a ligand or ligands in combination.



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